

EFFECTIVE CATALYST TO PRODUCE NAPHTHA FROM VACUUM GASOIL HYDROCRACKING AND DISCRETE LUMP MODELING

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## Abstract

A multi performance characteristics optimization based on Taguchi approach is proposed for Vacuum Gas Oil (VGO) hydrocracking process. Experimental runs have been planned as per Taguchi's principle with three important input parameters such as reaction time, temperature, and kind of catalyst. Results show that the kind of catalyst is the predominant variable for the desired performance characteristics. Discrete lumping model is developed to predict pseudo-components (gas, naphtha, kerosene, and diesel) produced during the process. Finally, a production model for the produced pseudo-components in the presence of the selected catalyst was formulated.

**Keywords:** : Vacuum gas oil; Hydrocracking, Catalyst; Naphtha; discrete lumping model.

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## 1. Introduction

To improve the quality of petroleum fuels, the environmental regulations have led to the development of hydrocracking process as the second important refining process. Hydrocracking is a catalytic cracking process for conversion of complex feedstocks, such as vacuum gas oils (VGO), into lighter and valuable products such as LPG, naphtha, kerosene, and diesel [1]. As the demand for light fuels is going to increase rapidly, the quality and yield of hydrocracking products have to be further improved to meet the future demands [2].

To understand more about hydrocracking of unconventional crude oils, information about the effect of reaction conditions on selectivity, conversion, and type of feedstock is essential. This information can be obtained either from experiments or by simulation. It should be considered that experiments are highly desired, but they are costly and time consuming. Simulations are usually very rapid and cheap to conduct. However, modeling hydrocracking of heavy oils is not an easy task, since it requires detailed characterization of products and feed, in contrast to other lighter petroleum streams, is more complex to perform due to the huge amount of heavy hydrocarbons present on its composition. An accurate kinetic model must be employed during the simulation of hydrocracking reactor. There are different approaches for modeling hydrocracking kinetics which have been recently reviewed by Ancheyta *et al.* [3]. Modeling kinetics of the reactions which are occurring during hydrocracking of petroleum feedstocks has been traditionally studied by discrete approximation, specifically by lumping compounds of feed and produced products into a few cuts which are characterized by ranges of normal boiling points (e.g. naphtha, middle distillates, residue, etc.), which undergo different series and parallel reactions [3]. The important advantages of the lumping technique are its easy computational implementation and a small amount of data required for parameter estimation. The more lumps, the better description, but increasing the number of lumps increases the number of parameters to be estimated [3]. In the lump modeling, compounds have been classified based on certain factors. These pseudo-components have a same molecular structure and classified based on different properties such as boiling point,

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molecular mass, a number of carbon atoms and so on [4]. Some examples of research done in this field are given as follows.

In 2013, Al-Humaidan *et al.* have investigated the effect of operating conditions (i.e., residence time and reaction temperature) on the quality of the products and yield. They also determined the kinetic parameters from the experimental data and compared them with each other [5]. Browning *et al.* based on analyzing results which are obtained from two-dimensional gas chromatography have developed a kinetic model for hydrocracking of a real VGO in a semi-batch reactor [6]. In 2014, Ignacio Elizalde and Jorge Ancheyta studied the kinetics of the hydrocracking of residue and catalyst deactivation by using the continuous kinetic lumping approach [7].

To simulate and design the behavior of heavy oil upgrading processes at commercial scale, adequate reactor modeling tools are required. The objective of this work is the development of a kinetic model based on experimental data, to account major VGO hydrocracking reactions capable of describing the behavior of both pilot and industrial scale reactors. The experiments were designed by Taguchi method to produce naphtha from VGO hydrocracking, and then the discrete lumping model of the selected catalyst is studied.

## 2. Reaction systems

### 2.1. Testing procedure of the catalysts in hydrocracking of VGO

Hydrocracking of n-hexadecane was conducted on a steel tubular fixed-bed down-flow reactor. The experimental setup was depicted in figure 1.

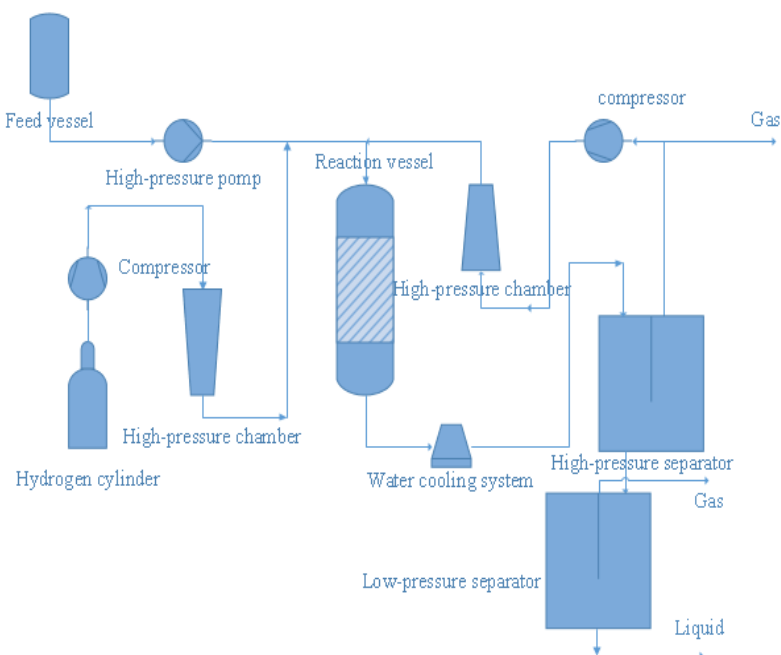


Figure 1. Schematic of the experimental setup

For each test, 1 gr catalyst was filled in the reactor and reduced by H<sub>2</sub> gas at 30 bar pressure and space velocity of 200 h<sup>-1</sup> with constant heating rate from ambient to 453 K and maintained at this temperature for 1 h. for pre-paring Ni-Mo-S phases, the catalysts were sulfided by a stream of 1wt% of dimethyl disulfide in hexane. Conditions of sulfidation were as follows: hydrogen atmosphere with an H<sub>2</sub>/Oil volumetric ratio of 80 nL/L at 30 bar and a space velocity of 200 h<sup>-1</sup>. Then, the samples were heated from 453 to 583 K with a constant heating rate of 0.5 K/min and kept at this temperature for 10 h. After the activation step, the performances of catalysts were evaluated using n-C<sub>16</sub> hydrocarbons. Conditions of the reaction are as

follows: Feed injection rate of 30 cm<sup>3</sup>/h and H<sub>2</sub>/Oil = 175 nL/L, 30 bar, WHSV = 3 kg/ (L·h), LHSV = 4.2 h<sup>-1</sup>. Physical and chemical properties of the feedstock are presented in table 1.

Table 1. Physical and chemical properties of the feedstock

Property	Feedstock	Property	Feedstock
Sp. Gr.	0.893	10 Vol%, °C	380
Viscosity @ 100°C	4.8	30 Vol%, °C	407
S, wt%	1.57	50 Vol%, °C	426
C7 insoluble wt%	0.12	70 Vol%, °C	443
Distillation	ASTM D-86	90 Vol%, °C	473
IBP, °C	250	95 Vol%, °C	489
5 Vol%, °C	356	100 Vol%, °C	506
Lumps of feed comp. (wt%)	Diesel	%10	
	VGO	%90	

## 2.2. Experimental Design method

The Taguchi method has been usually selected to optimize the design parameters [8] because this approach can strikingly minimize the overall experimental costs and the testing time. The optimum experimental conditions, using the orthogonal array can be determined by the Taguchi method, [9]. In this study, Taguchi model with L<sub>16</sub>(4<sup>3</sup>) orthogonal array was based on three controllable factors with four levels (Table 2).

Table 2. Factors and levels of each factor

Factor	Description	Level 1	Level 2	Level 3	Level 4
A	Catalyst	USY-ASA/Ni-Mo	USY-ASA/Ni-W	β-ASA/Ni-W	β-ASA/Ni-Mo
B	Temperature, (°C)	380	395	400	410
C	Reaction time, (hr.)	1	2	4	6

The analysis of the signal-to-noise (S/N) ratio is an important parameter in this model. Three usual types of S/N ratio analysis are as follows: (1) higher is better (HB), (2) nominal is best (NB), and (3) lower is better (LB) [9]. Since the target of this study is to maximize the naphtha cut produced from VGO hydrocracking using co-impregnated catalysts, the S/N ratio with HB characteristics is required, which is calculated by:

$$\frac{S}{N} = -10 \log \left( \frac{1}{n} \sum_{i=1}^n \frac{1}{Y_i^2} \right) \quad (1)$$

where: n is the number of repetitions which are under the same experimental conditions and Y is the measurement result.

The analysis of mean (ANOM) statistical approach is adopted herein to determine the optimal conditions. Initially, the mean of the S/N ratio of each controllable factor must be calculated at a certain level. For example,  $(M)_{Factor=I}^{Level=i}$ , the mean of the S/N ratio of factor I in level i, is given by:

$$(M)_{Factor=I}^{Level=i} = \frac{1}{n_{ii}} \sum_{j=1}^{n_{ji}} \left[ \left( \frac{S}{N} \right)_{Factor=I}^{Level=i} \right]_j \quad (2)$$

In Eq. (2),  $n_{ii}$  is the number of appearances of factor I in the level i,  $\left[ \left( \frac{S}{N} \right)_{Factor=I}^{Level=i} \right]_j$  is the S/N ratio of factor I in level i and  $j^{th}$  is its appearance sequence in Table 2. The analysis of variance (ANOVA) statistical method is also used to analyze the influence of each controllable factor under discussion process of VGO hydrocracking. The percentage contribution of each factor,  $\rho_F$ , is given by:

$$\rho_F = \frac{SS_F - (DOF_F V_{Er})}{SS_T} \times 100 \quad (3)$$

In Eq. (3),  $DOF_F$  is the degree of freedom of each factor, which is obtained by subtracting one from the number of the level of each factor (L). In equation (3) SST is the total sum of squares and given by:

$$SS_T = \sum_{(j=1)}^m (\sum_{(i=1)}^n Y_i^2) j - mn(\bar{Y}_T) \quad (4)$$

In equation (4),  $\bar{Y}_T$  is:

$$\bar{Y}_T = \left( \sum_{(j=1)}^m (\sum_{(i=1)}^n Y_i) j \right) \div mn \quad (5)$$

In equation (5), m represents the number of experiments carried out in this study, and n is the number of repetitions under the same experimental conditions. In equation (3) SSF is the factorial sum of squares and given by:

$$SS_F = \frac{mn}{L} \sum_{(k=1)}^L (\bar{Y}_K - \bar{Y}_T)^2 \quad (6)$$

Here  $\bar{Y}_K$  is the average value of the measurement results of each factor in the  $k_{th}$  level.

Furthermore, the variance of error,  $V_{Er}$ , is given by

$$V_{Er} = \frac{(SS_T - \sum_{(F=A)}^E SS_F)}{(m(n-1))} \quad (7)$$

In this research, the minimum applied temperature was set at 380°C, and the maximum temperature was set at 410°C. In temperatures above 500°C, all of the liquid feedstock can be converted into gas [10], on the other hand, at temperatures below 350°C; hydrocracking of VGO to the liquid product is ineffective. Reaction time is also an important factor in effectively designing catalytic process of hydrocracking [12], so it considered in this model investigation. The reason could be explained by the fact that when the reaction time exceeds the optimum time, the majority of the liquid feed will be converted into other products such as naphtha and gas [10]. Experiments designed using Taguchi method is listed in Table 3.

Table 3. Experiments design by Design-Expert software and Taguchi method

Test number	Factor A: catalyst	Factor B: Temperature, (°C)	Factor C: reaction time (hr.)
1	USY-ASA/Ni-Mo	380	1
2	USY-ASA/Ni-Mo	395	2
3	USY-ASA/Ni-Mo	400	4
4	USY-ASA/Ni-Mo	410	6
5	USY-ASA/Ni-W	380	2
6	USY-ASA/Ni-W	395	1
7	USY-ASA/Ni-W	400	6
8	USY-ASA/Ni-W	410	4
9	β-ASA/Ni-W	380	4
10	β-ASA/Ni-W	395	6
11	β-ASA/Ni-W	400	1
12	β-ASA/Ni-W	410	2
13	β-ASA/Ni-Mo	380	6
14	β-ASA/Ni-Mo	395	4
15	β-ASA/Ni-Mo	400	2
16	β-ASA/Ni-Mo	410	1

### 3. Kinetic model development

Hydrocracking models have significantly been developed over the last few decades [13]. A number of kinetic models have been suggested to hydrocracking process which has been composed of a limited number lumps (generally less than 10) [13-16]. These models can be used to simulate a small number of quantities which are important to the designer and/or operator of an HCK unit, such as naphtha yield [13]. Two different kinetic lumping models have been used to VGO hydrocracking reaction, (1) continuous and (2) discrete lumping models [17]. The kinetics of gas oil hydrocracking in a continuous fixed-bed tubular flow reactor was studied by Qader and Hill [4]. They found that rate of hydrocracking is of first order with respect to feed concentration [4]. The hydrocarbon mixture is studied in terms of a continuous assignment (i.e., in terms of boiling point) rather than being made up of discrete entities. Then, the reactivity of the hydrocarbon mixture is defined as a continuous function. This subject without an exponential increase in the number of parameters let a fine resolution of the distillation curve. Besides, it is possible to combine the continuous and discrete lumping approaches by defining more than one continuous distribution [18]. The Increase of computational capabilities and the availability of sophisticated analytical techniques (e.g. [19] and [20]) are caused to develop of microkinetic models for HCK of heavy petroleum fractions. In order to reduce the size of the reaction networks, computational algorithms have been made. The single event microkinetic modeling method was originally developed by Froment *et al.* [21]. Before a rigorous lumping model is performed, the single events coefficients [22-23] are calculated for each individual reaction in order to reduce the size of the network without loss in information.

#### 3.1. Discrete lumping model

##### 3.1.1. Models based on wide distillation range fractions

The kinetics of VGO hydrocracking was studied by Hill and Qader in a continuous fixed-bed tubular flow reactor [4, 14, 17]. They found that the rate of hydrocracking is followed by first order with respect to the concentration of feed [17] and activity energy of this reaction is about 21.1 kcal/mol. In this investigation, the kinetic data were obtained at 80 bar pressure, temperatures between [380-410°C], a constant H<sub>2</sub>/oil ratio of 5900 scfb. Then based on boiling point range of product, it was classified into LPG (0-39°C), naphtha (IBP- 150 °C), kerosene (IBP- 150-250°C) and diesel (IBP- 250-380 °C). In this investigation, it was observed that depend on temperature, hydrocracking of VGO using a catalyst has been followed by different models. In this letter, a discrete lumping model of the selected catalyst,  $\beta$ -ASA/Ni-W, is considered and changing procedure of their products during the hydrocracking process of VGO was formulated.

##### 3.1.1.1. Discrete lumping model of VGO hydrocracking in presence with $\beta$ -ASA/Ni-W catalyst

After conducting research on catalyst  $\beta$ -ASA/Ni-W, it was found that in temperatures 380°C this catalyst follows the model listed in Fig. 2. In this model, the four produced cut oils followed by parallel reactions.

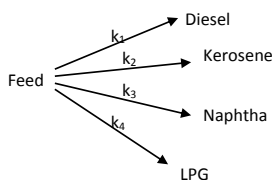


Fig. 2 Schematic of model 1 of hydrocracking process in parallel reactions

Attentive to one-degree kinetic of VGO hydrocracking, kinetic equations of this process in presence with the  $\beta$ -ASA/Ni-W catalyst are as follows. In this process, VGO was converted as equation 3:

$$-r_F = (k_1 + k_2 + k_3 + k_4)F \rightarrow \frac{dF}{dt} = -(k_1 + k_2 + k_3 + k_4)F \xrightarrow{t=0 \Rightarrow F=1} F = e^{-(k_1+k_2+k_3+k_4)t} \quad (3)$$

In mentioned process, the differential kinetic equation of the produced diesel cut follow of equation 4:

$$\frac{dD}{dt} = k_1F = k_1e^{-(k_1+k_2+k_3+k_4)t} \quad (4)$$

Kerosene was changing follows of equation 5:

$$\frac{dK}{dt} = k_2F = k_2e^{-(k_1+k_2+k_3+k_4)t} \quad (5)$$

The differential kinetic equation of produced naphtha follows of as equation 6:

$$\frac{dN}{dt} = k_3F = k_3e^{-(k_1+k_2+k_3+k_4)t} \quad (6)$$

The differential kinetic equation of the produced gas is followed of equation 7:

$$\frac{dG}{dt} = k_4F = k_4e^{-(k_1+k_2+k_3+k_4)t} \quad (7)$$

By this suppose that amount of gas, naphtha, kerosene and diesel were zero at first, solving above equations are as follows:

$$D = \frac{-k_1}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1+k_2+k_3+k_4)t} + \frac{k_1}{(k_1 + k_2 + k_3 + k_4)} \quad (8)$$

$$K = \frac{-k_2}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1+k_2+k_3+k_4)t} + \frac{k_2}{(k_1 + k_2 + k_3 + k_4)} \quad (9)$$

$$N = \frac{-k_3}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1+k_2+k_3+k_4)t} + \frac{k_3}{(k_1 + k_2 + k_3 + k_4)} \quad (10)$$

$$G = \frac{-k_4}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1+k_2+k_3+k_4)t} + \frac{k_4}{(k_1 + k_2 + k_3 + k_4)} \quad (11)$$

In above equations, kinetic constants,  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$ , was calculated by fitting between experiment data and the equations [8-11] by Levenberg-Marquart algorithm. After considering experimental data in temperatures between 395-410°C, it could be found this catalyst don't follow the model depicted in Fig. 1. So, another model (Fig. 3) was proposed to explain the performance of the catalyst and changing procedure of different oil cuts.

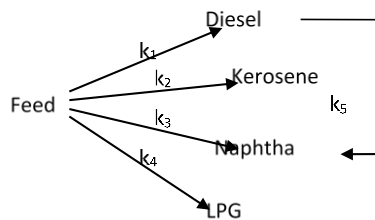


Fig. 3 Schematic of model 2 of hydrocracking process

Kinetic equations of oil cuts during VGO hydrocracking are as follows:

$$-r_F = (k_1 + k_2 + k_3 + k_4)F \xrightarrow{t=0 \Rightarrow F=1} F = e^{-(k_1+k_2+k_3+k_4)t} \quad (12)$$

Diesel is changed during two steps. In step (1) diesel is produced from VGO conversion and (2) converted into naphtha. Differential kinetic equation of diesel is as follows:

$$\frac{dD}{dt} = k_1 F - k_5 D \tag{13}$$

At this model, Kinetic equation of kerosene is as follows:

$$\frac{dK}{dt} = k_2 F \tag{14}$$

Kinetic equation of naphtha is:

$$\frac{dN}{dt} = k_3 F + k_5 D \tag{15}$$

Kinetic equation of gas is:

$$\frac{dG}{dt} = k_4 F \tag{16}$$

By this suppose that initial amount of gas, naphtha, kerosene, and diesel were zero, solving above equations are:

$$D = \left( \frac{k_1}{(k_5 - (k_1 + k_2 + k_3 + k_4))} \right) \left( e^{-(k_1 + k_2 + k_3 + k_4)t} - e^{-k_5 t} \right) \tag{17}$$

$$K = \frac{-k_2}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1 + k_2 + k_3 + k_4)t} + \frac{k_2}{(k_1 + k_2 + k_3 + k_4)} \tag{18}$$

$$N = \left( \frac{-k_3}{(k_1 + k_2 + k_3 + k_4)} \right) e^{-(k_1 + k_2 + k_3 + k_4)t} + \tag{19}$$

$$\left( \frac{k_1 k_5}{(k_5 - (k_1 + k_2 + k_3 + k_4))} \right) \left( \left( \frac{e^{-k_5 t}}{k_5} \right) - \left( \frac{e^{-(k_1 + k_2 + k_3 + k_4)t}}{(k_1 + k_2 + k_3 + k_4)} \right) \right) + \left( \frac{k_3}{(k_1 + k_2 + k_3 + k_4)} \right) - \left( \frac{k_1 k_5}{(k_5 - (k_1 + k_2 + k_3 + k_4))} \right) \left( \left( \frac{1}{k_5} \right) - \left( \frac{1}{(k_1 + k_2 + k_3 + k_4)} \right) \right) \tag{20}$$

$$G = \frac{-k_4}{(k_1 + k_2 + k_3 + k_4)} e^{-(k_1 + k_2 + k_3 + k_4)t} + \frac{k_4}{(k_1 + k_2 + k_3 + k_4)}$$

## 4. Results and discussion

### 4.1. Results from Taguchi method

Using Taguchi method in this research, 16 experiments (Table 2) were chosen to consider a suitable catalyst from among four catalysts,  $\beta$ -ASA/Ni-Mo,  $\beta$ -ASA/Ni-W, USY-ASA/Ni-Mo, and USY-ASA/Ni-W, to grow conversion of VGO and naphtha cut produced during the process. Results of these experiments and S/N of them were calculated using equation (1) and listed in Table 4.

To choose an appropriated choice for each factor in conversion in Taguchi method, the amount of  $(M)_{Factor=1}^{level=i}$  (equation 2) was calculated, and the optimum condition for enhancing conversion of VGO hydrocracking is achieved. Using Minitab software, yield and S/N of VGO conversion were calculated in optimum condition and listed in Table 5.

Table 4 Results of experiments designed and S/N of them calculated using equation 20

Test number	Conversion %	S/N	naphtha %	S/N
1	3.936	11.9369	0.44	-7.05799
2	11.3066	20.6455	1.6666	3.83324
3	26.4279	28.8168	4.6096	13.9044
4	51.7	34.2796	12.2	21.6265
5	7.42	17.4549	0.8	-1.64193
6	5.376	14.9477	0.783	-1.89061
7	35.8901	31.2487	6.52452	16.8119
8	40.75	31.6680	9.4	18.4112
9	38.76	31.9946	15.3	24.1038
10	74.7	37.6170	40.4	32.4866
11	24.599	27.1801	13.733	21.6413
12	59.3486	35.7290	37.7	31.8719
13	53.6	34.2737	23.4	26.6051
14	55.722	34.8526	27.716	28.8649
15	41.84	32.5453	21.6	26.6511
16	30.25	29.8785	17.65	25.7418

Table 5. Optimum condition for conversion of VGO hydrocracking

Optimum condition	catalyst	Temperature (°C)	Reaction time (hr.)	Yield (%wt.)	S/N
Conversion	$\beta$ -ASA/Ni-W	410	6	78.6333	43.4901

S/N curve of conversion of VGO hydrocracking is depicted based on reaction factors by Taguchi method. This figure comes in Fig. 4:

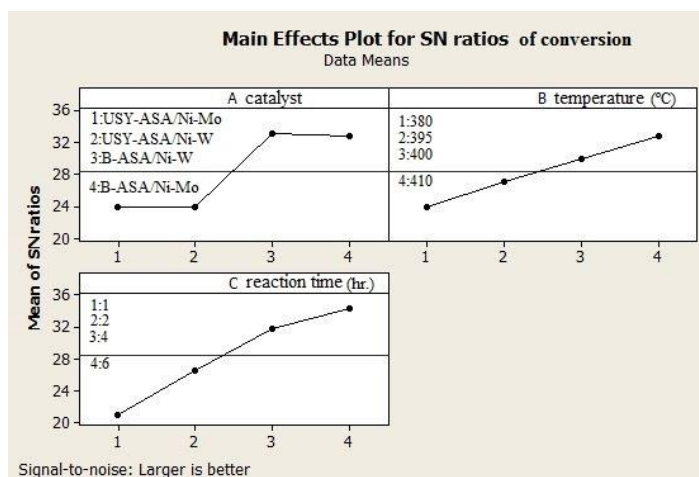


Fig. 3. Conversion of VGO during hydrocracking in different reaction time and temperature

Based on Fig. 4, as time and temperature of reaction are increased, the amount of VGO conversion is increased. This could be because the hydrocracking reaction is done more with increasing temperature and reaction time. This subject is in accordance with references [10] and [24]. In comparison with two catalysts, USY-ASA/Ni-W and USY-ASA/Ni-Mo, the amount of VGO conversion was very much when  $\beta$ -ASA/Ni-W and  $\beta$ -ASA/Ni-Mo catalysts were used in this process. Since USY and  $\beta$  are two different zeolites which have two different crystallites and since crystallite of the catalyst is much important factor affected the performance of catalyst, and this is in accordance with reference [25], it could be said that crystallite of two both catalysts could be caused by the difference between amount conversion of VGO. By comparing the performance of two catalysts,  $\beta$ -ASA/Ni-W and  $\beta$ -ASA/Ni-Mo, in VGO hydrocracking, it could be said that capability of W metal in VGO hydrocracking is more amount than that of Mo metal. This should be by reason of the difference of electron properties of W



and Mo. To choose a suitable choice for each factor in producing naphtha, the amount of  $(M)_{Factor=1}^{level=i}$  (equation 21) is calculated. optimum conditions for producing naphtha is listed in Table 6. Using Minitab software, yield and S/N of naphtha in this condition were calculated.

Table 6 the optimum condition for producing naphtha during VGO hydrocracking

Optimum condition	catalyst	Temperature (°C)	Reaction time (hr.)	Yield (%wt.)	S/N
Conversion	B-ASA/Ni-W	410	6	41.0759	37.4115

S/N Produced naphtha is depicted in different factors. This is depicted in Fig. 5:

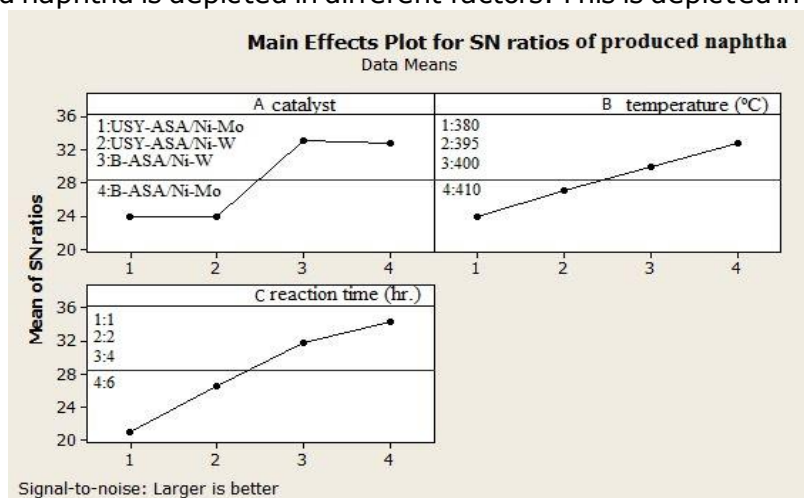


Fig. 4. Produced naphtha during VGO hydrocracking in different reaction time and temperature

According to above, as reaction time and temperature were increased, the amount of produced naphtha was increased. This subject could be approved that when the temperature is increased, production of light products is increased [26], in other hand; kerosene and diesel produced are decreased. This subject could be approved that hydrocracking of VGO is thermally controlled [24]. In VGO hydrocracking, the amount of produced naphtha was increased when  $\beta$ -ASA/Ni-W or  $\beta$ -ASA/Ni-Mo were used as a catalyst; this subject could be due to crystallite of  $\beta$  zeolite because crystallite of the catalyst has an effective impact on the performance of catalyst [25]. These observations showed that effect of W metal should be more than Mo in producing naphtha from VGO hydrocracking. This could be because of different electronic properties of these two metals. Obtained results approved that although temperature and resistance times are very important parameters an effective parameter to produce a certain cut from VGO hydrocracking should be kind of catalyst.

#### 4.2. Results from modeling VGO hydrocracking

Obtained experimental data from VGO hydrocracking in temperature 380°C, when  $\beta$ -ASA/Ni-W catalyst was used, have been listed in Table 7:

Table 7 Experimental data obtained from VGO hydrocracking using  $\beta$ -ASA/Ni-W catalyst in temperature 380°C

Time(hr.)	Temperature (°C)	Gas (%wt.)	Naphtha (%wt.)	Kerosene (%wt.)	Gas oil (%wt.)
1	380	0.19	1.32	2.16	3.66
2	380	0.39	2.47	4.18	6.9
4	380	0.82	4.76	7.77	12.83
6	380	1.098	6.5	10.6	17.864

It was observed, in 380°C temperature, the production model pseudo-components (gas, naphtha, kerosene, and diesel) during VGO hydrocracking has been followed by model 1. Based on this figure, it could be said that in this temperature diesel, kerosene, naphtha, and gas produced during VGO hydrocracking were followed by four parallel reactions and equations. This subject has also come in references [27] and [17]. Kinetic equations (3-11) describe kinetic behavior of this catalyst in 380°C. Kinetic constants,  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$ , of these equations, were calculated by fitting between experiment data and the equations using the Levenberg-Marquart algorithm. These Kinetic constants,  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$ , were listed in Table 8.

Table 8 Kinetic constants calculated by fitting experimental data obtained from VGO hydrocracking using  $\beta$ -ASA/Ni-W catalyst in temperature 380°C

Temperature (°C)	$k_1$	$k_2$	$k_3$	$k_4$
380	0.0281	0.0329	0.0484	0.0124

Changing procedure of each pseudo-components produced during VGO hydrocracking in the presence of the  $\beta$ -ASA/Ni-W catalyst in 380°C were shown in Fig. 6:

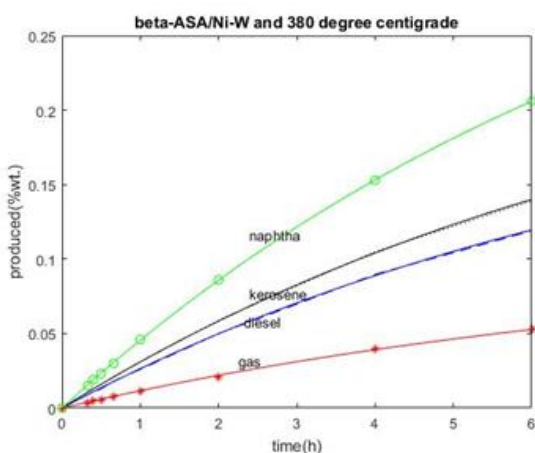


Fig. 5 Procedure of changing of products produced during VGO hydrocracking using  $\beta$ -ASA/Ni-W catalyst at 380°C

Fig. 6 shows that produced naphtha during the process is more amount than other products, in other words, it could be said that this catalyst is selective to produce naphtha and this result is in accordance with what is reported previously [28].

The amount of gas, kerosene, and diesel produced in the process was less than naphtha. In temperature range 395-410°C, it was found that behavior of this catalyst wasn't followed by parallel reactions, in other words, diesel produced from VGO hydrocracking could be converted into naphtha. This model could approve that the catalyst,  $\beta$ -ASA/Ni-W, is selective to produce naphtha. Experimental data in this temperature range are listed in Table 9:

Table 9 Experimental data obtained from VGO hydrocracking using  $\beta$ -ASA/Ni-W catalyst in temperature range 395-410°C

Time (hr.)	Temperature (°C)	Gas (%wt.)	Naphtha (%wt.)	Kerosene (%wt.)	Gas oil (%wt.)
1	395	2.3	10.733	4.75	2.3
2	395	4.3	19.466	8.6	4.2
4	395	6.8	31.85	14.07	6.7
6	395	8.2	40.4	17.7	8.4
1	400	3.3	13.733	5.2	2.366
2	400	5.9	23.966	9.0	4.132
4	400	9.2	38.08	14.1	6.03
6	400	11.1	46.5	17.4	7.6
1	410	6.116	22.35	4.9833	1.9
2	410	10.132	37.7	8.5666	2.95
4	410	14.3	54.8	11.93	2.975
6	410	16.3	62.1	13.7	3

Between temperature ranges 395-410°C, changing procedure of each pseudo-component produced during VGO hydrocracking using  $\beta$ -ASA/Ni-W catalyst is shown in Fig. 7:

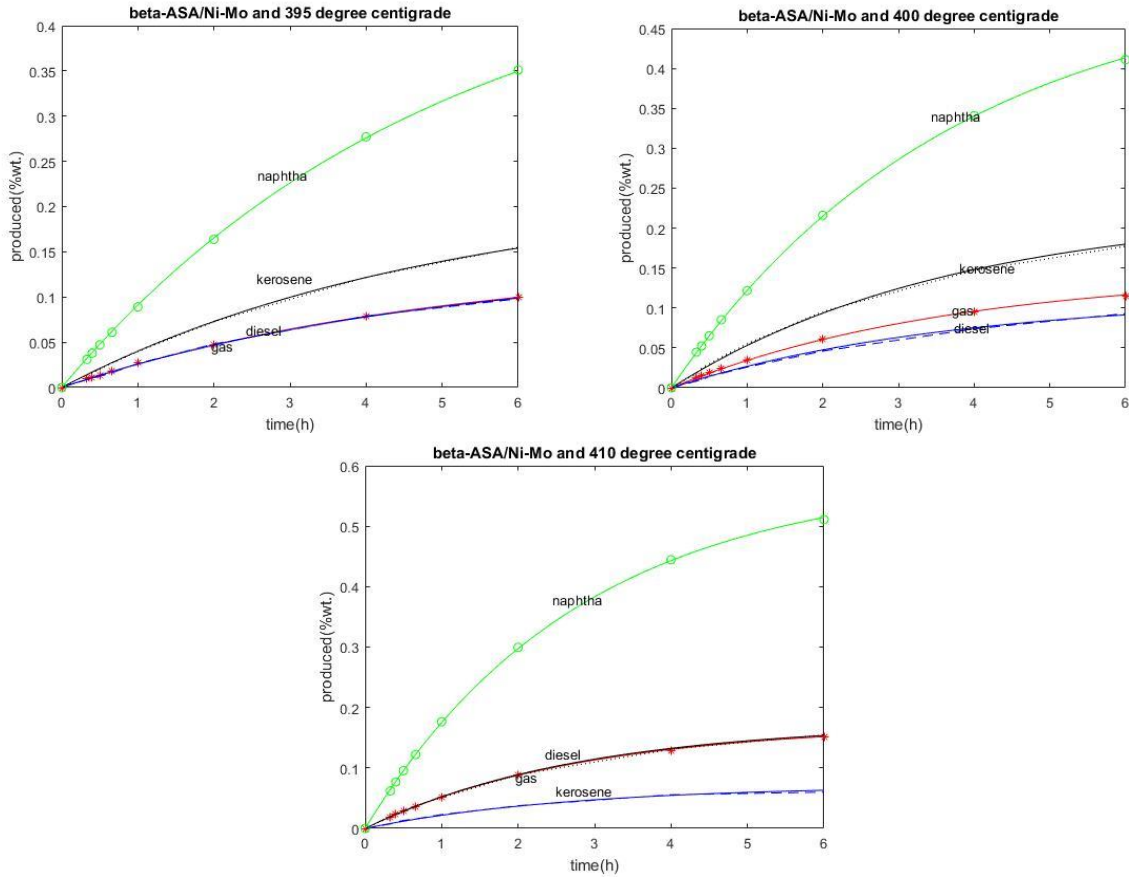


Fig. 6 Procedure of changing of products produced during VGO hydrocracking using  $\beta$ -ASA/Ni-W catalyst in temperature range 395-410°C

Based on data obtained in temperature range 395-410°C (Table 4-7), it could be found that VGO hydrocracking was followed by the model showed in Fig. 2 and equations (12-20). Kinetic constants,  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$ , and  $k_5$ , of these equations in the presence of this catalyst, were calculated by fitting experiment data and the equations using the Levenberg-Marquart algorithm. These Kinetic constants,  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$ , and  $k_5$ , are listed in Table 10.

Table 10. Kinetic constants calculated by fitting experimental data obtained from VGO hydrocracking using  $\beta$ -ASA/Ni-W catalyst in temperature range 395-410°C

Temperature (°C)	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$
395	0.027	0.0536	0.1205	0.0254	0.0207
400	0.0282	0.0593	0.157	0.0382	0.0315
410	0.0296	0.0637	0.2781	0.0762	0.2539

According to Arrhenius equation (19), Arrhenius constants ( $k_0$ ) and activation energy ( $E_a/R$ ) of VGO hydrocracking were calculated and listed in Table 11:

Table 11. Arrhenius constants ( $k_0$ ) and activation energy ( $E_a/R$ ) of VGO hydrocracking using  $\beta$ -ASA/Ni-W catalyst

I=lump No.	$K_{0i}$ (1/hr)	$E_{i/R}$ (°K)
1	1.588833	2719.1
2	94.59456	4982.8
3	4.95E+15	25566
4	9.8E+19	33199
5	3.83E+49	78996

As it is shown in Fig. 6, it could be found that with increasing temperature, the amount of naphtha produced during VGO hydrocracking is increased and amount of the produced diesel is decreased when  $\beta$ -ASA/Ni-W catalyst is used in this process. This subject could be approved the fact that diesel could be converted into naphtha as the temperature is increased. Obtained results approved that conversion of VGO into lighter products (i.e., gas, naphtha, kerosene, and diesel) is thermally controlled [24]. It is also shown that whatever temperature is increased, naphtha is increased, in other word; diesel could more be converted into naphtha. According to the trend of changing diesel with the temperature in Fig. 6, it could be said that amount of produced gas is increased with time and temperature.

## 5. Validation of the model

First according to experiment data the parameters affected by the process were properly estimated and adjusted with the one-degree kinetic reaction of VGO hydrocracking. then kinetic equations of the process were written. Good agreement was observed between experimental and predicted values. Average deviation was also lower than 5% for the total set of operating conditions. An analysis of residuals was conducted, and the results are showed in Fig. 6 and 5. All these results approve that the values of the optimized model parameter, their dependence with temperature in the range 380-410°C, and in general the discrete kinetic model represent a good compatibility with experimental data curve of heavy oil distillation hydrocracking.

## 6. Conclusion

In this investigation, a multi performance characteristics optimization based on Taguchi approach is proposed for Vacuum Gas Oil (VGO) hydrocracking process. Experimental data obtained in presence of four catalysts,  $\beta$ -ASA/Ni-Mo,  $\beta$ -ASA/Ni-W, USY-ASA/Ni-Mo and USY-ASA/Ni-W, and different conditions; pressure 80bar, four temperatures (380°C, 395°C, 400°C, 410°C) and eight reaction times (0.33, 0.4, 0.5, 0.667, 1, 2, 4, 6 hr), were analyzed by design expert software and Taguchi method. The production model was based on temperature and time and kinetic constants of discrete lumping equations and calculated by experimental data and Levenberg-Marquardt algorithm. As a result of this investigation, it should be proposed that effect of the  $\beta$ -ASA/Ni-W catalyst on conversion of VGO and producing light products (i.e., gas and naphtha) during the hydrocracking process is more than those of  $\beta$ -ASA/Ni-Mo, USY-ASA/Ni-W, and USY-ASA/Ni-Mo.

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